Research article

Sabine Scholz (née Lehmann), Manuel Serif, David Schleheck, Martin D.J. Sayer, Alasdair M. Cook and Frithjof Christian Küpper*

Sulfoquinovose metabolism in marine algae

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Abstract: This study aimed to survey algal model organisms, covering phylogenetically representative and ecologically relevant taxa. Reports about the occurrence of sulfonates (particularly sulfoquinovose, taurine, and isethionate) in marine algae are scarce, and their likely relevance in global biogeochemical cycles and ecosystem functioning is poorly known. Using both field-collected seaweeds from NW Scotland and cultured strains, a combination of enzyme assays, high-performance liquid chromatography and matrix-assisted laser-desorption ionization time-of-flight mass spectrometry was used to detect key sulfonates in algal extracts. This was complemented by bioinformatics, mining the publicly available genome sequences of algal models. The results confirm the widespread presence of sulfonates and their biosynthetic pathways in macro- and microalgae. However, it is also clear that catabolic pathways, if present, must be different from those documented from the bacterial systems since no complete cluster of gene homologues of key genes could be detected in algal genomes.

Keywords: *Ectocarpus*; *Flustra foliacea*; isethionate; sulfoquinovose; taurine.

1 Introduction

Sulfonates are widespread both as xenobiotic compounds and natural products, yet knowledge about the biosynthesis of the latter remains limited. Biotechnological interest in sulfonates relates to their property as surfactants (Singh et al. 2007; Van Hamme et al. 2006) and the need for their biodegradability due to their widespread application and entry into the environment (Kertesz and Wietek 2001). Benson and colleagues isolated a sulfolipid from higher plants and photosynthetic microorganisms, including the unicellular green algae *Chlorella* and *Scenedesmus* and the purple nonsulfur bacterium *Rhodospirillum* (Benson et al. 1959). The polar head group was identified as sulfoquinovose (SQ, Figure 1) and the structure of the sulfolipid was elucidated as sulfoquinovosyldiacylglycerol (SQDG; Benson 1963; Daniel et al. 1961). SQ is produced in quantities estimated at some 10 billion tonnes annually (Goddard-Borger and Williams 2017). Its biosynthesis in photosynthetic organisms has recently been reviewed. The available evidence is consistent with the biosynthesis of SQDG from uridine diphosphate (UDP)-glucose and sulfite in a two-step process via UDP-SQ (Goddard-Borger and Williams 2017). It turned out that SQDG plays a significant role in the biological sulfur cycle, where it can represent up to 50% of sulfur in plants and green algae. Especially in photosynthetic plant tissues, SQDG concentrations of 1–6 mM are observed (Benson 1963). In general, the estimated value for global biosynthesis of SQDG is about 3.6×10^{10} tons per year (Harwood and Nicholls 1979). It has long been thought that SQDG plays a role in photosynthesis because of its general occurrence in plants but also in photosynthetic bacteria and some flagellates (Harwood and Nicholls 1979). However, many photosynthetic bacteria almost or entirely lack the compound, whereas SQDG is found in several non-photosynthetic organisms. For example, it has been found in the symbiotic soil bacterium *Sinorhizobium meliloti* (Cedergren and Hollingsworth 1994) and in eggs and sperm cells of the sea urchin *Pseudocentrotus depressus* (Isono

Sabine Scholz (née Lehmann) and Manuel Serif contributed equally to this work.

***Corresponding author: Frithjof Christian Küpper**, Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland, UK; and Present address: School of Biological Sciences, Cruickshank Bldg, University of Aberdeen, St. Machar Drive, Aberdeen AB24 3UU, Scotland, UK, E-mail: fkuepper@abdn.ac.uk
Sabine Scholz (née Lehmann) and Manuel Serif, Department of Biology, University of Konstanz, D-78457 Konstanz, Germany; and Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland, UK
David Schleheck and Alasdair M. Cook, Department of Biology, University of Konstanz, D-78457 Konstanz, Germany
Martin D.J. Sayer, NERC National Facility for Scientific Diving, Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland, UK; and Tritonia Scientific Ltd., Dunstaffnage Marine Laboratories, Dunbeg, Oban, Argyll, PA37 1QA, Scotland, UK

et al. 1967). Analysis of mutants lacking SQDG biosynthesis suggested that SQDG has no essential role in photosynthesis but rather acts as a surrogate for anionic phospholipids during phosphate limitation and is required for proper protein import into chloroplasts (Benning 1998; Güler et al. 1996). The conclusion was that SQDG is required for chloroplast stabilization and function (Yu and Benning 2003). As already mentioned, SQDG concentrations are high in plant cells, thus it does not seem surprising that it also serves as an internal sulfur source for protein biosynthesis during sulfur starvation in *Chlamydomonas reinhardtii* (Sugimoto et al. 2007). Analytical methods in use for the detection and analysis of SQDG include thin-layer chromatography (TLC), nuclear magnetic resonance (NMR) spectroscopy, gas chromatography (GC)–mass spectrometry (MS) following saponification and derivatization, and tandem mass spectrometric methods (reviewed by Goddard-Borger and Williams 2017).

At this point, considering its abundance in nature, the question arises as to how the sulfolipid, or at least SQ, is degraded? Two major sulfoglycolytic pathways have been discovered in recent years for SQ degradation, the sulfo-Embden–Meyerhof–Parnas (sulfo-EMP) and sulfo-Entner–Doudoroff (sulfo-ED) pathways, which mirror the major steps in the glycolytic EMP and ED pathways. Sulfoglycolysis produces C3-sulfonates, which undergo biomineralization to inorganic sulfur species, completing the sulfur cycle (Goddard-Borger and Williams 2017). The catabolism of SQDG to SQ involves a rapid hydrolysis by plant acyl hydrolases to form the deacylated product sulfoquinovosylglycerol (SQG, Figure 1, reaction 1; Benson 1963; Shibuya et al. 1963), which is further attacked by β-galactosidase yielding SQ (Figure 1, reaction 2; Shibuya and Benson 1961). Roy and colleagues proposed an SQ degradation pathway based on the consideration that SQ is an analogue of glucose 6-phosphate (Roy et al. 2003), and Denger and colleagues identified the genes, enzymes and intermediates of the core pathway of bacterial degradation of SQ in *Escherichia coli* K-12 MG1655 to quantitative amounts of 2,3-dihydroxypropane-1-sulfonate (DHPS), which is completely degraded by other bacteria under aerobic as well as anaerobic conditions (Burrichter et al. 2018; Denger et al. 2014; Figures 2, 3). Another bacterial pathway involves SQ-dehydrogenase which has been found in *Pseudomonas putida* SQ1 (Felux et al. 2015) and quantitatively excretes 3-sulfolactate. The latter is also degraded by other bacterial communities (Denger et al. 2012; Rein et al. 2005). A third pathway has been described recently, involving a 6-deoxy-6-sulfofructose trans-aldolase step in *Bacillus* spp. and other *Firmicutes* bacteria (Frommeyer et al. 2020; Liu et al. 2020).

As little free SQ was observed in plant extracts, the compound appeared to be readily metabolized in the plant cell (Benson 1963). Furthermore, sulfolactate, DHPS, sulfolactaldehyde and presumably cysteate from SQDG were detected in the green alga *Chlorella* (Shibuya et al. 1963). SQDG has furthermore been observed in red algae of the genus *Gracilaria* (Araki et al. 1990) and in several brown algae including *Ishige okamurai*, *Colpomenia sinuosa*, *Endarachne binghamiae*, *Scytosiphon lomentaria*, *Undaria pinnatifida*, *Eisenia bicyclis*, *Dictyota dichotoma*, *Pachydictyon coriaceum*, *Padina arborescens*, *Hizikia fusiformis*, *Sargassum horneri*, *S. ringgoldianum* and *S. thunbergii* (Araki et al. 1991). Isethionate (Ise) is found at high concentrations (<0.001–1.70% dry weight) in red algae (Barrow et al. 1993; Holst et al. 1994). In the red alga *Grateloupia turuturu*, isethionate has been reported to inhibit the settlement of *Balanus amphitrite* cyprid larvae (Hellio et al. 2004). While taurine occurs only in traces in the plant kingdom, sea weeds have relatively high concentrations (0.01% of wet weight; Huxtable 1992). Although taurine and presumably

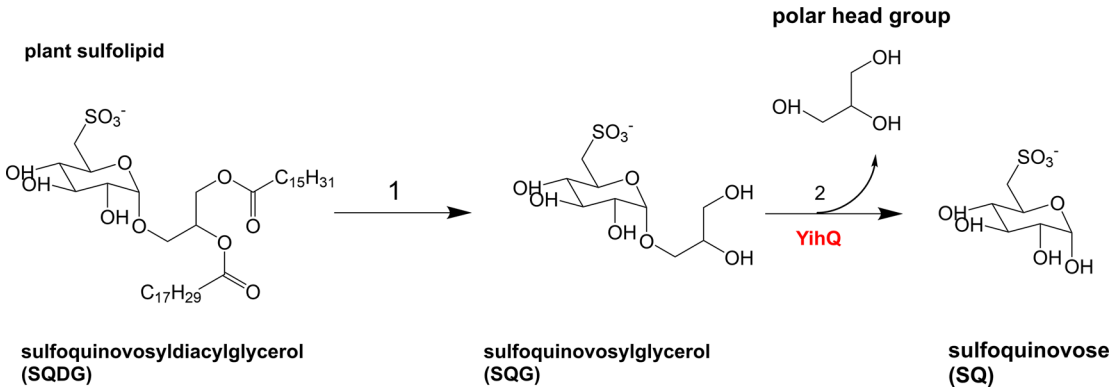

Figure 1: Catabolism of the plant sulfur lipid sulfoquinovosyldiacylglycerol to sulfoquinovose in *Escherichia coli* K-12 MG1655, based upon Denger (2014).

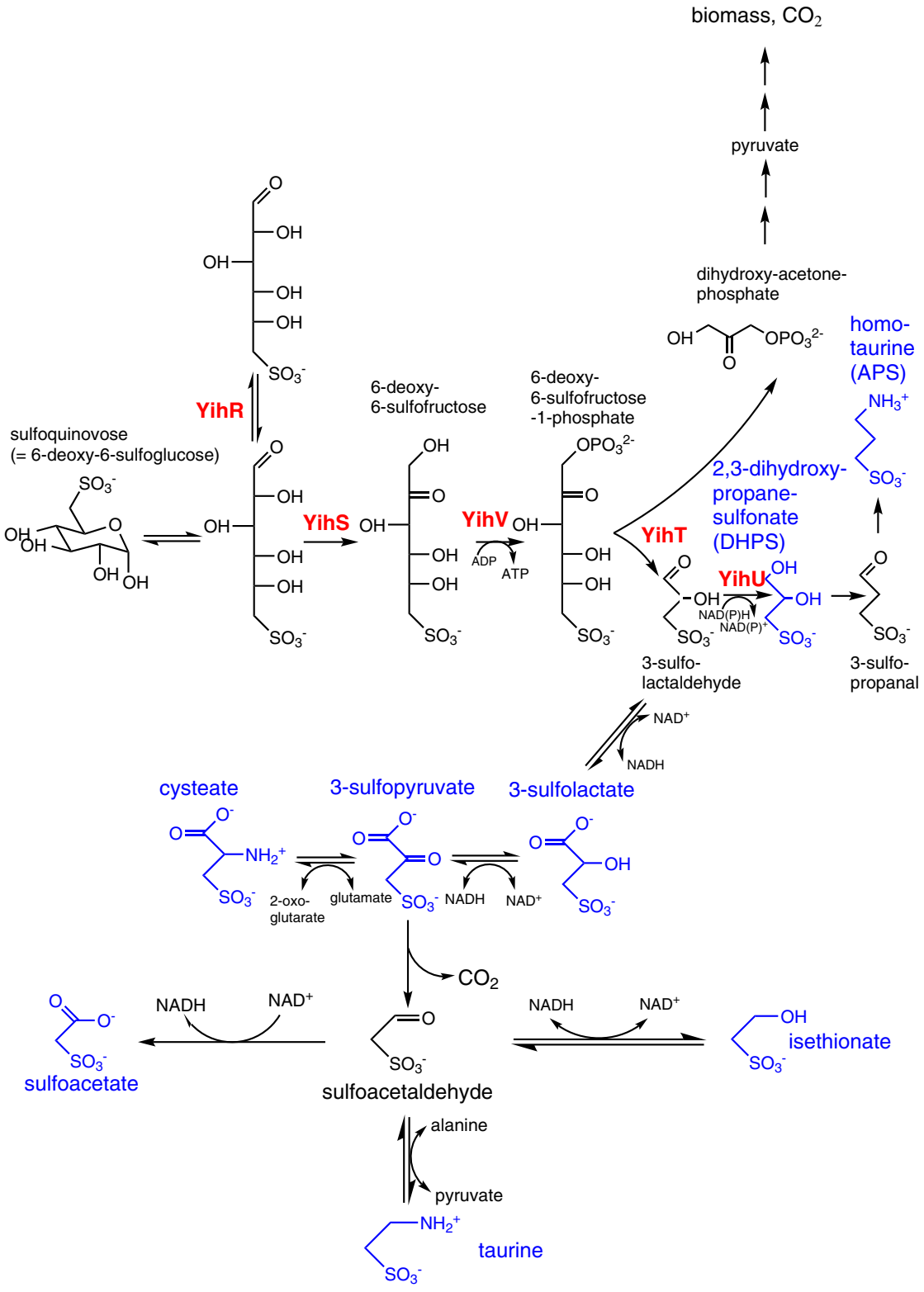

Figure 2: The unknown algal metabolism converting sulfoquinovose (SQ) to 3-sulfolactaldehyde (SLA) and to other known algal products. The intermediates which were found in this study are marked in blue. The algal enzymes involved are unknown; thus we used established pathways from bacteria. Reaction: 1, SLA reductase (Denger et al. 2014); 2, hypothetical dehydratase; 3, APS transaminase (Mayer and Cook 2009); 4, SLA dehydrogenase (Felux et al. 2015); 5, SuL dehydrogenase (Rein et al. 2005); 6, SuP decarboxylase (ComDE) (Rein et al. 2005); 7, isethionate reductase (Krejčík et al. 2010; Peck et al. 2019); taurine transaminase (Laue and Cook 2000; Peck et al. 2019), 9, SAA dehydrogenase (Krejčík et al. 2008).

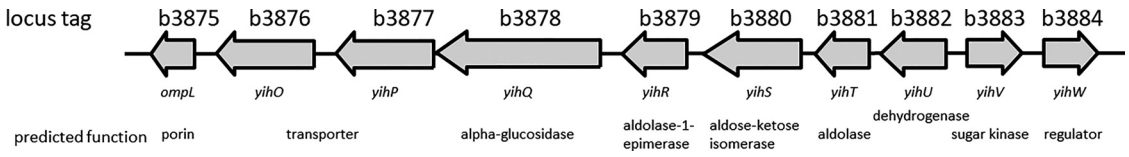

Figure 3: Enterobacterial sulfoglycolysis, according to Denger (2014).

isethionate have several physiological functions, including osmoprotection and intracellular calcium level modulation (e.g. Schaffer et al. 2003), these sulfonates could also be considered as intermediates or end products in SQ metabolism (Figure 2).

Marine algae are of paramount importance in various biogeochemical cycles. In addition to the role of carbon storage in climate regulation (Krause-Jensen et al. 2018), marine biodiversity is, in part, controlled through biogeochemical cycling by marine biota. For example, the emission of sulfur-based gases in the coastal zone (Burdett et al. 2015) may contribute to climate regulation (for example stabilising climate; Charlson et al. 1987) and kelp forests have a major role in the transfer of iodine from the ocean to the atmosphere (Küpper and Kamenos 2018; Küpper et al. 2011). There is also a strong and growing interest in seaweeds for biotechnological use and the sustainable development of coastal regions and island territories (Cornish et al. 2020), such as the French Overseas Territories (Stiger-Pouvreau and Zubia 2020). However, in general, we know very little about the occurrence of sulfonates in marine algae (other than the aforementioned report of isethionate in a red alga; Hellio et al. 2004) and other marine life, and reports (e.g. of a sulfonated siderophore from a marine bacterium; Hickford et al. 2004) are sporadic at best. In this study, we further explored the potential occurrence of sulfoglycolysis in various algal lineages, by confirming the presence of SQ metabolites in field-collected red, green and brown algae, as well as in strains of the Culture Collection of Algae and Protozoa (CCAP) of very diverse phylogenetic background. Furthermore, we investigated the distribution of the bacterial gene cluster for SQ biosynthesis and for sulfoglycolysis in algae, which was greatly facilitated by the numerous algal genomes which have become available over the last 10–15 years, including the first-ever sequenced seaweed, the brown alga *Ectocarpus siliculosus* (Cock et al. 2010), the diatoms *Thalassiosira weissflogii* (Armbrust et al. 2004) and *Phaeodactylum tricornutum* (Bowler et al. 2008), the red alga *Chondrus crispus* (Collen et al. 2013) and the unicellular green alga *Chlamydomonas rheinhardtii* (Merchant et al. 2007).

2 Materials and methods

2.1 Chemicals

Standard chemicals were of the highest purity available and purchased from Sigma-Aldrich, Roth, Merck or Fluka. 2,3-dihydroxypropane-1-sulfonate was synthesized by Dr. Thomas Huhn (Department of Chemistry, University of Konstanz) as described in Mayer et al. (2010).

2.2 Organisms, growth, harvesting of cells and preparation of cell-free extracts

Microalgae (a 1-l batch culture for each strain, see Table 1) were provided by the CCAP (Culture Collection of Algae and Protozoa; Gachon et al. 2007), Dunstaffnage, Scotland. The cultures were grown in a Thermo-818 Illuminated incubator at 18 °C with 14:10 light/dark cycle at an irradiance of 80 µmol m^{-2} s^{-1}. Care was taken to use nutrient media not containing detectable traces of sulfonates (based on manufacturers' information).

Macroalgae were collected in the vicinity of Dunstaffnage (near Oban, Scotland; 56°28.9N; 05°30.1W) by snorkelling and two dives in May 2010 (Table 2). They were among the most common seaweed taxa of the area, easy to recognize, with identifications confirmed where necessary (Bunker et al. 2012). Fresh algae were quickly rinsed with seawater and stored frozen at −20 °C before analysis. At least three entire thalli were collected of each species, subsequently cleaned from macroscopically visible epiphytic animals and algae, and then pooled for bulk extraction.

Two strains of *Cupriavidus* were used to prepare membrane fractions for the enzyme assays used for determining isethionate and DHPS, since these strains are known to contain the enzymes catalyzing these metabolic steps (Mayer and Cook 2009; Mayer et al. 2010). Furthermore and potentially relevant in the present context, *Cupriavidus necator* is known to produce the siderophore cupriachelin when associated with algae (Kurth et al. 2019). *C. necator* H16 and *C. pinatubonensis* JMP134 were grown aerobically at 30 °C in a phosphate-buffered mineral salt medium, pH 7.2 (Thurnheer et al. 1986). Either 10 mM isethionate or 10 mM DHPS (2,3-dihydroxypropane-1-sulfonate) served as sole added carbon or energy source, respectively. Precultures (3 ml, 50 ml) were grown in 30/300 ml screw-cap tubes or Erlenmeyer flasks on a roller or a shaker. Cultures for enzyme assays or protein purification (1 l in 5-l Erlenmeyer flasks) were harvested in the mid-exponential phase of growth (OD_{580nm} 0.5–0.6) by centrifugation (13,000*g*, 20 min, 4 °C), washed twice with 50 mM phosphate buffer (supplemented with 2.5 mM $MgCl_2$) and disrupted (after adding DNaseI (50 µg ml^{-1}) in a French pressure cell as previously described (Junker et al. 1994). Cell debris was removed by centrifugation (17,000*g*, 5 min, 4 °C), the resulting

Table 1: List of the cultures analyzed, including the culture collection accession number, the GenBank accession number, and the media which were used for batch cultures.

Species	Class	Strain Accession No.	GenBank Accession No.	Media	Dry weight
Lingulodinium polyedra (F.Stein) J.D.Dodge	*Dinophyceae*	CCAP 1121/2	EU532474	K	0.1 g
Scrippsiella trochoidea (F.Stein) A.R.Loeblich III	*Dinophyceae*	CCAP 1134/8	n.a.	K	0.1 g
Rhodomonas salina (Wislouch) D.R.A. Hill *et* R. Wetherbee	*Cryptophyceae*	CCAP 978/24	EU926158	K	0.5 g
Coccolithus pelagicus Bown	*Prymnesiophyceae*	CCAP 913/3	AF196307	f/2	0.1 g
Chaetoceros debilis Cleve	*Bacillariophyceae*	CCAP 1010/6	FR865489	f/2 + Si	0.1 g
Ectocarpus siliculosus (Dillwyn) Lyngbye	*Phaeophyceae*	CCAP 1310/4	CABU00000000	Modified Provasoli-half strength	0.5 g
Paralia sulcata (Ehrenberg) Cleve	*Bacillariophyceae*	CCAP 1059/2	n.a.	f/2 + Si	0.1 g
Skeletonema costatum (Greville) Cleve	*Bacillariophyceae*	CCAP 1077/1C	FR865518	f/2 + Si	0.22 g
Skeletonema marinoi Sarno *et* Zingone	*Bacillariophyceae*	CCAP 1077/5	n.a.	f/2 + Si	0.2 g

supernatant was designated as a crude extract. The cells were ultracentrifuged to obtain the membrane fraction (17,000*g*, 60 min, 4 °C). The supernatant was designated as a soluble fraction and the cell pellet (washed twice with phosphate buffer) as a membrane fraction.

2.3 Extraction of algae

To analyse different species of algae for any intermediates of sulfoglycolysis, extracts were generated using the speed extractor E-916 (Büchi, Flawil, Switzerland) following the user manual (Supplementary Table S1) using analytical grade methanol. First, samples were weighed, then freeze-dried, then weighed again and homogenized (2.5 g dry weight [DW] macroalgae or 0.1–0.5 g DW microalgae; cf. Table 1) with diatomaceous earth (provided by the manufacturer) to a final weight of 5 g. For macroalgae, a column size of 40 ml was used, while 20-ml columns were used for microalgae. The extracts were collected in 250-ml flasks and were evaporated to dryness on a vacuum evaporator (375 mbar, 2 h). Residues were re-dissolved in ethyl acetate/distilled water (1:1 v/v). The ethyl acetate phase was extracted three times with distilled water. The aqueous solutions (45 ml) were further analysed for sulfonates either using enzymatic endpoint methods or by high-performance liquid chromatography (HPLC), ion chromatography (IC), or matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements (all repeated in triplicate). The procedure had been found to be robust against loss of metabolites during extraction over many years (Cook and Schleheck unpublished). Normalization was based on DW algal biomass.

2.4 Enzyme purification and enzymatic endpoint method

The enzymatic endpoint method, according to Bergmeyer et al. (1986) was used to screen for isethionate or DHPS. To measure isethionate, we used the membrane fraction of *C. necator* H16 in which the membrane-bound *IseJ* (isethionate dehydrogenase) is localized. The enzyme assay was carried out as previously described (Weinitschke et al. 2010). To determine DHPS concentrations, *Hps*N (DHPS 3-dehydrogenase) was purified from *Cupriavidus pinatubonensis* JMP134, following Mayer et al. (2010). The quantitative analyses of the algae were repeated three times.

2.5 Analytical methods

Bacterial growth was followed as turbidity (OD_{580nm}). Protein in bacterial extracts was assayed by protein-dye binding (Bradford 1976). For detection of taurine, homotaurine ((3-aminopropane-1-sulfonate) homotaurine, APS) and cysteate, algal extracts were derivatized with dinitrofluorobenzene and quantified after separation by HPLC (Denger et al. 1997; Laue et al. 1997). HPLC was conducted with Beckman HPLC instruments and with C18 columns made by Knauer using our established methods (Mayer and Cook 2009). Using ion chromatography with suppression, we screened for isethionate, sulfoacetate and sulfolactate (Denger et al. 2004; Styp von Rekowski et al. 2005). All DHPS and isethionate standards were dissolved in water. 1-Fluoro-2,4-dinitrobenzene (DNFB) derivatives could be quantified with high sensitivity (0–100 µM), and DHPS as well (0–100 µM). Derivatised samples (amino groups with DNFB) were detected at 360 nm.

Furthermore, MALDI-TOF-MS analysis in the negative ion mode was conducted to establish the presence of sulfonates. The samples were analyzed by MALDI-TOF mass spectrometry using a Microflex LRF mass spectrometer (Bruker Daltonics), equipped with a 335-nm nitrogen laser and operated in the reflector mode (resolution approx. 15,000). As a matrix, a saturated solution of HCCA (α-hydroxycinnamic acid) in a solution of 80% acetonitrile and 20% water, with the addition of 0.1% trifluoroacetic acid, was used. External calibration in a positive ion mode was carried out with a peptide calibration standard, ranging from 1500 to 3500 Da. For sample preparation, 1 µl of the matrix solution was mixed with 1 µl of the sample solution and 1 µl of the mixture was spotted on the MALDI target. 200 to 500 single shots were summed to generate the final MS spectrum. The quantitative analyses of algal materials were repeated three times.

Table 2: Analysis of algal extracts and their indicated intermediates of sulfoglycolysis.

Algal species	Phylum	Sulfonates detected (%, DW)		
		Taurine	DHPS	APS
Ceramium sp.	*Rhodophyta*	n.d.	n.d.	0.02
Delesseria sanguinea (Hudson) J.V.Lamouroux	*Rhodophyta*	n.d.	0.04*	n.d.
Dilsea edulis Stackhouse	*Rhodophyta*	0.09*	n.d.	n.d.
Heterosiphonia japonica Yendo	*Rhodophyta*	n.d.	n.d.	0.05
Heterosiphonia sp.	*Rhodophyta*	0.07	n.d.	0.05
Hypoglossum sp.	*Rhodophyta*	n.d.	n.d.	0.02
Odonthalia dentata (Linnaeus) Lyngbye	*Rhodophyta*	n.d.	0.05*	n.d.
Palmaria palmata (Linnaeus) Weber *et* Mohr	*Rhodophyta*	0.08	0.05	0.03
Phycodrys rubens (Linnaeus) Batters	*Rhodophyta*	n.d.	n.d.	0.05
Plocamium cartilagineum (Linnaeus) P.S. Dixon	*Rhodophyta*	0.09*	0.05*	n.d.
Polyneura sp.	*Rhodophyta*	n.d.	n.d.	n.d.
Porphyra sp.	*Rhodophyta*	n.d.	0.02*	n.d.
Alaria esculenta (Linnaeus) Greville	*Phaeophyceae*	n.d.	n.d.	n.d.
Desmarestia aculeata (Linnaeus) J.V.Lamouroux	*Phaeophyceae*	n.d.*	0.03*	n.d.
Fucus serratus L.	*Phaeophyceae*	0.05	n.d.	0.12
Laminaria hyperborea (Gunnerus) Foslie	*Phaeophyceae*	n.d.	n.d.	0.05
Saccharina latissima C.E.Lane, C.Mayes, Druehl *et* G.W.Saunders	*Phaeophyceae*	n.d.	n.d.	n.d.
Ulva sp.	*Chlorophyta*	n.d.	0.02*	n.d.
Flustra foliacea L.	*Bryozoa, Metazoa*	0.49	n.d.	n.d.
Lingulodinium polyedrum (F.Stein) J.D.Dodge	*Alveolata*	0.12*	0.02*	n.d.
Scrippsiella trochoidea (F.Stein) A.R.Loeblich III	*Alveolata*	0.03*	0.03*	n.d.
Rhodomonas salina (Wislouch) D.R.A.Hill *et* R.Wetherbee	*Cryptophyta*	0.02	0.02	n.d.
Coccolithus pelagicus Bown	*Haptophyceae*	0.04	0.02*	n.d.
Chaetoceros debilis Cleve	*Stramenopiles*	n.d.	0.02*	n.d.
Ectocarpus siliculosus (Dillwyn) Lyngbye	*Stramenopiles*	n.d.	0.02	n.d.
Paralia sulcata (Ehrenberg) Cleve	*Stramenopiles*	0.1*	0.02*	0.1
Skeletonema costatum (Greville) Cleve	*Stramenopiles*	n.d.	0.03*	n.d.
Skeletonema marinoi Sarno *et* Zingone	*Stramenopiles*	n.d.	0.02*	n.d.

Asterisks (*) highlight the intermediates proofed by MALDI-TOF-MS analysis. APS, (3-aminopropane-1-sulfonate) homotaurine; DHPS, 2,3-dihydroxypropane-1-sulfonate; DW, dry weight; n.d., not detected.

2.6 Genomics and bioinformatics

Protein sequences of sulfoquinovose degradation gene clusters from *E. coli* K12 and *P. putida* SQ1 were BLASTed against the PhycoCosm database (Nordberg et al. 2014) of the Joint Genome Institute (JGI, https://phycocosm.jgi.doe.gov/phycocosm/home) on 9 April 2020. For each protein, the best hit for each organism was chosen (Supplementary Table S3). An E-value cut-off of 1 E-5, minimum coverage of 50% and a minimum% identity of 35 was chosen. Sequences containing only small regions of homology which do not correspond to a complete protein domain were excluded.

3 Results and discussion

3.1 Determination and quantification of isethionate

With the approaches available to us and despite reports of isethionate in red algae (Hellio et al. 2004; Holst et al. 1994), only traces of isethionate were detected in the algal extracts investigated in this study. Using the enzymatic endpoint method, two problems were encountered. Firstly, IseJ was not stable enough for reliable enzyme assay. Secondly, this method is not sensitive enough to screen for isethionate in algal extracts. Thus, it was decided to use ion chromatography to analyse isethionate (also for sulfoacetate, sulfopyruvate and sulfolactate). However, it was impossible to detect any sulfonate in the extracts reliably because of interference from high chloride concentrations, but it may well have been present at low concentrations.

3.2 Sulfonates detected in macro- and microalgae

To analyse the extracts for intermediates of sulfoglycolysis we used HPLC (cysteate, taurine, APS; Supplementary Table S2) and a chromatographically purified fraction of HpsN for an enzymatic endpoint method (DHPS) and confirmed their presence by MALDI-TOF-MS analysis (Supplementary Figure S1).

Among the Rhodophyta, at least one of the intermediates could be detected in significant amounts in all species, except *Polyneura* (Table 2). The concentration range of taurine was around 0.08% (DW, dry weight) in dry algae, a value which is higher than previously reported concentrations (*Gelidium subcostatum*: 0.0125% of wet weight, *Grateloupia elliptica*: 0.025% of wet weight; Kataoka and Ohnishi 1986). In general, we found higher concentrations of taurine than of DHPS or APS. Although APS is a known natural product of marine red algae

(e.g. Ito et al. 1977; Miyazawa et al. 1970) and DHPS is a widespread plant intermediate (Shibuya and Benson 1961) that is excreted by all diatoms (Benson and Lee 1972), no concentrations were given in these reports. Compared to red algae, the concentrations of sulfonated intermediates were lower in brown algae. This is in line with the observations by Harnedy and FitzGerald (2011). In two brown algae, we could not find any of the sulfonates, but in some samples (*Desmarestia aculeata*, *Fucus serratus*, *Laminaria hyperborea*) we found DHPS, taurine, and APS, which was confirmed by MALDI-TOF-MS in representative cases. In *F. serratus*, we measured taurine (0.05% DW) and APS (0.12% DW), with the concentration of the latter being remarkably high.

The only representative of the Chlorophyta investigated was *Ulva* sp. Here, we detected DHPS (0.02% DW) which was confirmed by MALDI-TOF-MS analysis.

For comparison, we also investigated the bryozoan *Flustra foliacea*, which belongs to the Metazoa family. In extracts of this species, we found extraordinarily high taurine concentrations (0.49% DW); however, millimolar concentrations have been reported from mammals (Jacobsen and Smith 1968).

Interestingly, all microalgal cultures from CCAP tested contained DHPS, which could be confirmed by MALDI-TOF-MS analysis in most cases. Here, the average concentration was 0.02% in dried algae, which is slightly lower compared to the macroalgae. We found APS only in one sample (*Paralia sulcata*) but in a very high concentration (0.1% DW). This alga also contained high levels of taurine (0.1% DW). Another microalga showing similarly high taurine concentrations (0.12% DW) was *Lingulodinium polyedrum*.

In general, it can be stated that the most abundant sulfonate detected in macro- and microalgal extracts was taurine. None of the extracts contained measurable amounts of cysteate, which supports the idea that 3-sulfopyruvate is directly decarboxylated to sulfoacetaldehyde (SAA; Figure 2). Furthermore, two other amino acids could be detected in *Palmaria palmata*, glutamic acid and alanine (4.8% of dry alga), which were confirmed by co-chromatography. For this alga, it is known that, especially during late winter and spring, high concentrations of glutamic acid, serine, and alanine are detectable (Galland-Irmouli et al. 1999).

In general, the protein concentration of marine algae is dependent on species and season. Thus, it is conceivable that concentrations of other compounds are affected by seasonality. This is well documented, e.g. for iodine in kelp (Ar Gall et al. 2004) and the interaction of kelp with the surrounding seawater (Gonzales et al. 2017), for polyphenols in the brown alga *Ascophyllum nodosum* (Parys et al. 2009) and mycosporine-like amino acids and pigments (Lalegerie et al. 2020) as well as ash (15–27% of DW), proteins (14–30% of DW) and the low molecular weight carbohydrate floridoside (Rødde et al. 2004) in the red alga *P. palmata*. Rhodophyta usually contain higher protein levels relative to dry weight compared to Chlorophyta and Phaeophyceae. An explanation for the higher taurine concentrations in our extracts could be the concise heating time for extraction (three times for 5 min).

3.3 Bioinformatic analysis of genes for degradation of SQ in algae

Two different degradation pathways for sulfoquinovose are known: An Embden–Mayerhof–Parnas type pathway identified in *E. coli* K12 (Denger et al. 2014) and an Entner–Doudoroff type pathway identified in *P. putida* SQ1 (Felux et al. 2015). The *yih*-cluster in *E. coli* (Figure 3) does not occur in sequenced algae (Supplementary Table S3a). The aldolase gene *yihT*, which encodes one of the key enzymes of the degradation pathway, was completely absent. Only potential homologs of the SQG glucosidase gene *yihQ* and the SLA reductase gene *yihU* could be found in several species with sequence coverage over 80% and a sequence identity of 30–40%. For the other genes, either no hits or only genes with up to around 50% sequence identity (in the case of *yihS* and *yihV*) were found in only one or two algal species. Thus, we do not believe there is support for the presence of the SQ Embden–Meyerhof–Parnas pathway in algae.

BLAST searches for the Entner–Doudoroff type SQ degradation pathway from *P. putida* showed potential homologs for several genes of the pathway (Supplementary Table S3b), including the 3-sulfolactaldehyde (SLA)-dehydrogenase gene PpSQ1_00088, the SG-dehydratase gene PpSQ1_00089, the SQ-dehydrogenase gene PpSQ1_00090_in the majority of the algal species analysed with coverages of 70–98% and identity of 30–55%. The SGL-lactonase gene PpSQ1_00091, the SQG-glucosidase gene PpSQ1_00094_and the aldolase gene PpSQ1_00100 were found only in a smaller subset of algal genomes. While no complete gene cluster was identified, candidate genes for several key enzymes of the pathway were present in several algal species.

4 Conclusions

While candidate genes for several key enzymes, namely for the *alpha*-glucosidase and for the aldolase of the Entner–

Doudoroff type pathway, were identified, these were present in only a smaller subset of algal species. Therefore, SQ degradation is most likely to follow other, as yet unknown, pathways in most algal species. Also, sulfoquinovose metabolism, which is well understood in bacteria, may be also highly dependent on the interactions between algal species and their microbiota, especially for catabolism. Bacteria were inevitably present both in the algal cultures and the field-collected algae used for this study. It would have been impossible to obtain the biomass required for this study, covering a similar taxonomic breadth, from axenically grown strains. In this context, further studies should attempt to use axenic strains of selected taxa. However, they should also consider how the microbial epibiome of algae and their joint metabolome affects aspects of SQ metabolism and other metabolic pathways of the sulfonates reported here. It has to be highlighted that the scope of this study was a first, and thus inherently preliminary, qualitative survey of the occurrence of sulfoquinovose metabolism in a very wide phylogenetic range of algae – ecophysiology and life history stages were not considered. Thus, different nutrient media had to be applied due to the very different requirements of model strains across such a wide phylogenetic diversity. Taken together, these factors limit the direct comparability of the data between species presented here.

The genetic data confirm the widespread presence of the SQ biosynthetic pathway in macro- and microalgae, and the chemical analyses confirm the metabolism to synthesize a number of sulfonates. Many bacterial pathways could serve as model systems for the reaction products observed in algae (Figures 2 and 3). However, there seems to be little evidence to support the degradation of SQ *via* a pathway homologous the *E. coli* SQ Embden–Meyerhof–Parnas pathway in a phylogenetically wide range of algae (and, likewise, a phylogenetically wide range of eukaryotes in general, cf. Supplementary Table S3) since only possible homologues for some selected enzymes have been identified in the present study.

Indeed, the bioinformatics results presented here highlight that catabolic pathways, if they exist, must be different from those documented from bacterial systems since no complete cluster of gene homologues of key enzymes could be found in algal genomes. A different hypothesis that could be derived from this finding is that the alga itself does not accomplish SQ catabolism and is not fully encoded by an algal genome. Instead, it requires a tight association with specific bacteria that could complement catabolic pathways, which are only partially present in algae.

Overall, sulfonates are more widespread in marine algae than previously thought, which may also contribute to the explanation of the widespread abundance of sulfonate-degrading bacteria in marine and coastal habitats (Durham et al. 2015; Tralau et al. 2011).

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Bionotes

Sabine Scholz (née Lehmann)
Department of Biology, University of Konstanz, D-78457 Konstanz, Germany
Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland, UK

Sabine Scholz (née Lehmann) got her PhD in 2013 from the University of Konstanz. Within this framework and working in the lab of Prof. Alasdair MacLeod Cook, she has explored the metabolism of sulfonates in microbes, marine algae and invertebrates from the angle of biochemistry, analytical chemistry and molecular biology.

Manuel Serif
Department of Biology, University of Konstanz, D-78457 Konstanz, Germany
Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland, UK

Manuel Serif started studying microalgae during his PhD at University of Konstanz, where he focused on the molecular characterization of blue-light dependent transcription factors called Aureochromes. He likes to improve upon and establish new genome editing methodologies in order to elucidate how diatoms adapt to changing light conditions on a molecular level.

Martin D.J. Sayer
NERC National Facility for Scientific Diving, Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland, UK
Tritonia Scientific Ltd., Dunstaffnage Marine Laboratories, Dunbeg, Oban, Argyll, PA37 1QA, Scotland, UK

Martin D.J. Sayer is the owner and managing director of Tritonia Scientific Ltd., a diving company based near Oban on the west coast of Scotland, that evolved from the UK National Facility for Scientific Diving in 2018. He obtained his PhD at the University of Wales studying the physiology of intertidal fishes. In 1991 he was appointed as a fisheries biologist at the Dunstaffnage Marine Laboratory before becoming head of the scientific diving unit in 1998. Martin has been involved with scientific diving for over 40 years and has supported numerous underwater research programmes around the World.

Alasdair M. Cook
Department of Biology, University of Konstanz, D-78457 Konstanz, Germany

Alasdair M. Cook retired from the Chair of Microbial Ecology at the University of Konstanz after holding positions at the ETH Zürich, Cornell University, and the University of Göttingen, having obtained his PhD at Glasgow University. The thrust of his work was biodegradation of *s*-triazines, phosphonates, LAS and natural sulfonates. The latter work developed to the elucidation of pathways, characterisation of enzymes and their genes, and the identification of the bacteria involved.

Frithjof Christian Küpper
Scottish Association for Marine Science, Oban, Argyll, PA37 1QA, Scotland, UK
Present address: School of Biological Sciences, Cruickshank Bldg, University of Aberdeen, St. Machar Drive, Aberdeen AB24 3UU, Scotland, UK
fkuepper@abdn.ac.uk

Frithjof Christian Küpper has held the Chair in Marine Biodiversity at the University of Aberdeen since 2011, after 8 years at the Scottish Association for Marine Science (Oban) as a Lecturer and Reader, studying the biodiversity and biochemistry of marine plants/algae. He conducted graduate studies at Roscoff and Konstanz for a joint French-German PhD. His research found that iodide serves as an inorganic antioxidant in kelp, the first described from a living system, impacting atmospheric and marine chemistry. A certified scientific diver, Frithjof has worked in the Mediterranean, South Atlantic (Ascension, Falkland Islands), Antarctica, the Arctic and the Arabian Gulf.